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13. ABSTRACT (Maximum 200 words)
THE OBJECTIVES OF THIS RESEARCH ARE TO CONDUCT LABORATORY EXPERIMENTS THAT WILL PREDICT THE PHOTOCHEMICAL AND BIOLOGICAL TRANSFORMATIONS OF DCPD AND DIMP IN THE SOILS AND WATERS OF ROCKY MOUNTAIN ARSENAL AND WILL PROVIDE A SEMIQUANTITATIVE EVALUATION OF DECOMPOSITION RATES OF AND PRODUCTS RESULTING FROM DCPD AND DIMP. DURING OCTOBER, ANALYTICAL METHODS WERE DEVELOPED TO DETERMINE CONCURRENTLY METHYLPHOSPHONATE (MP) AND ISOPROPYLMETHYLPHOSPHONATE (IMP) IN THE PRESENCE OF DIMP. THE PHOTOCHEMISTRY OF DCPD IN NATURAL WATERS WAS INVESTIGATED, AND MICROBIAL STUDIES OF 14C-LABELED DCPD AND DIMP WERE INITIATED.

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STUDIES OF ENVIRONMENTAL FATES OF DIMP AND DCPD

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INTRODUCTION

The U.S. Army Medical Bioengineering Research and Development Laboratory has the responsibility of developing environmental standards for pollutants that contaminate the environment at Army installations. Two such pollutants at the Rocky Mountain Arsenal (RMA) are dicyclopentadiene (DCPD) and diisopropylmethylphosphonate (DIMP).

The objectives of this research are to conduct laboratory experiments that will predict the photochemical and biological transformations of DCPD and DIMP in the soils and waters of Rocky Mountain Arsenal and will provide a semiquantitative evaluation of decomposition rates of and products resulting from DCPD and DIMP.

PROGRESS

During October, analytical methods were developed to determine concurrently methylphosphonate (MP) and isopropylmethylphosphonate (IMP) in the presence of DIMP. The photochemistry of DCPD in natural waters was investigated, and microbial studies of ^{14}C-labeled DCPD and DIMP were initiated.

Analytical Chemistry

Analytical methods were developed to determine MP and IMP, two expected transformation products of DIMP, in the presence of DIMP. Methyl-8® (dimethylformamide, dimethyl acetal) and Methelute® (trimethylanilinium hydroxide) were evaluated as methylating agents to convert these compounds to derivatives that lend themselves to gas chromatographic analysis. Methelute was found to be the superior reagent, yielding quantitative methylation and little chromatographic interference. The methyl derivatives of MP and IMP (as well as trimethylphosphate, an added cometabolite) were resolved from DIMP by use of capillary gas chromatography and alkali-flame ionization detection, as shown in Figure 1.

Photochemistry

In improving our experimental procedures to alleviate the problem of volatility in photolysis experiments, we found that very little, if any, photolysis of DCPD occurs in distilled water. Samples of DCPD at 2 ppm in distilled water were photolyzed for 110 hours in a

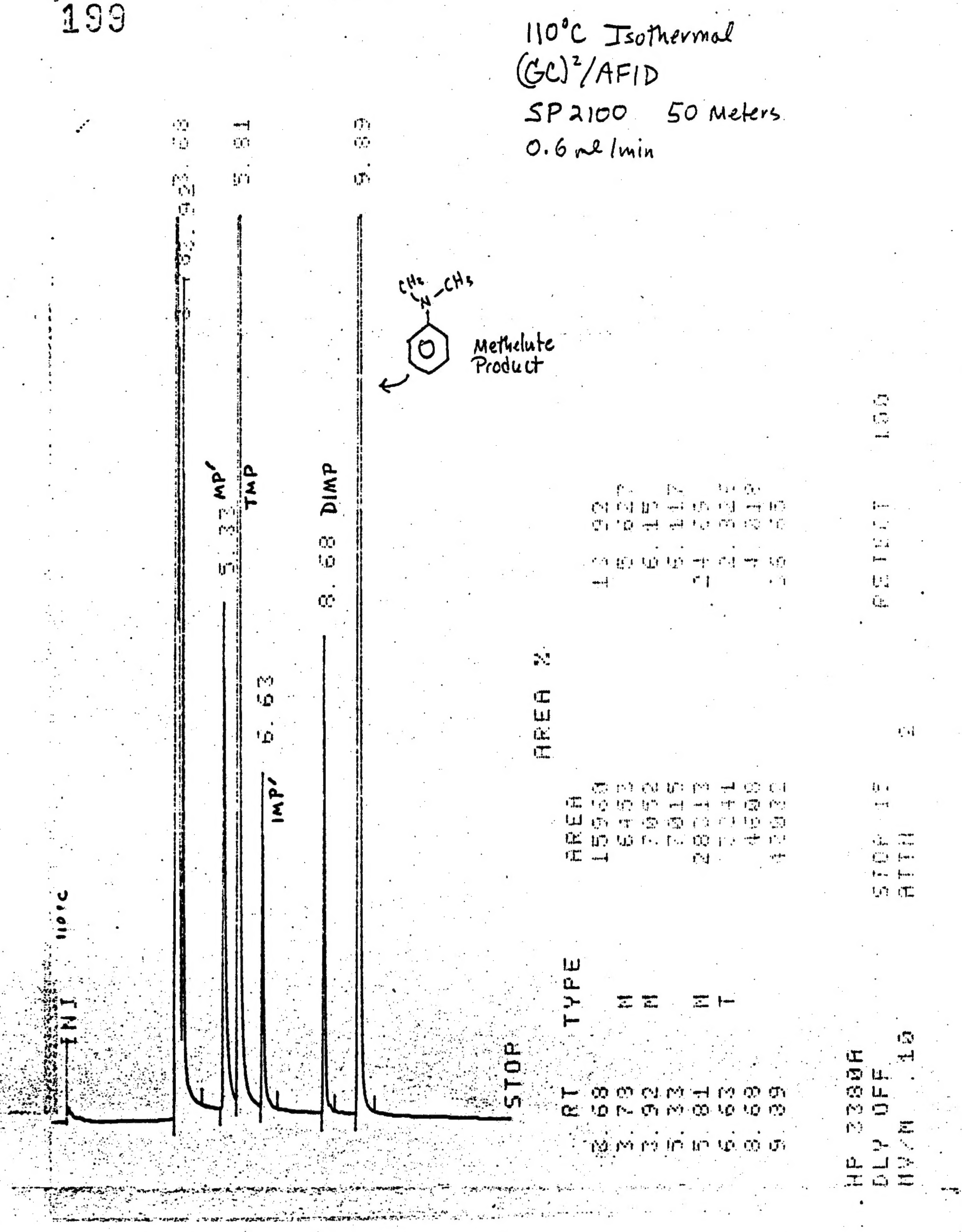


Figure 1 GAS CHROMATOGRAPHIC SEPARATION OF DIMP, TMP, and THE METHYL DERIVATIVES OF IMP AND MP

mercury light merry-go-round reactor. DCPD concentrations changed less than 2.0% relative to controls during that time.

The photolysis of DCPD (2 ppm) was also investigated in deep natural water obtained from Rocky Mountain Arsenal. After 94 hours of photolysis, an average loss of 32.2 ± 2.2% (0.34%/hr) was observed compared with controls. We are conducting another experiment to obtain a more detailed kinetic profile of this photolysis. Table 1 presents the data obtained to date.

Table 1

PHOTOLYSIS OF DCPD IN NATURAL RMA WATER

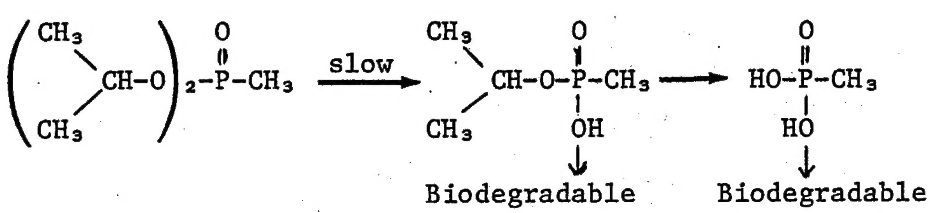
Time, ΔT	Loss of DCPD (%)	Rate (% hr^{-1})
24	17.1	0.71
48	26.4	0.55
101	35.3	0.35
48 control	0	

These results indicate that naturally occurring organics (such as humic acids) may be participating in the phototransformation of DCPD, acting either as singlet oxygen $^1O_2$ sensitizers or free radical oxidation initiators. These mechanisms are currently under investigation.

Biodegradation

The acclimation of DCPD- and DIMP-biodegrading organisms from RMA North Bog water and Palo Alto sewage plant effluent is continuing. However, after 7 weeks of acclimation, no transformation of either compound has been detected.

In phosphate-deficient medium, microbes from both RMA and Palo Alto sewage effluent were found to utilize MP, IMP, and trimethylphosphate readily. This indicates that the rate-limiting step is the initial transformation of DIMP, assuming that transformation occurs by a "hydrolysis" type of mechanism (Eq. 1).



(1)

IMP and MP were added as co-metabolic substrates to assist DIMP transformation, but no co-metabolism has been observed to date.

Our preliminary studies of DIMP biodegradation in soil have been initiated. ^{14}C-DIMP was added to RMA and local soils (moistened with water), and the generated $^{14}CO_2$ was trapped in KOH solution. After 1 week, indications of radioactivity appeared in the KOH trap. However, when the CO_2 was precipitated with barium ion and the $BaCO_3$ was washed with water and ethanol, most of the activity was found in the supernatants. We are investigating whether this activity results from ^{14}C-DIMP contamination or from volatile metabolites generated by the soil organisms.

The same phenomenon has been observed with ^{14}C-DCPD in soil studies. Radioactivity is observed in KOH traps but, barium precipitation of CO_2 incorporates little activity in barium carbonate. Because of its volatility, DCPD and possibly its volatile metabolites may accumulate in these traps. These possibilities are currently under investigation.

FUTURE WORK

Our future plans are to continue investigating DCPD and DIMP biotransformation using labeled compounds both in soil and liquid media. We also will investigate local eutrophic water samples for the development of DCPD- and DIMP-degrading organisms.

The photochemical studies will continue with the investigation of the photolysis of DCPD in natural waters as well as the initiation of solar photolysis studies in deep and shallow RMA waters.

Exhibit A is the performance schedule for project tasks, and Exhibit B is a graph of expenditures to date.

EXHIBIT A PERFORMANCE SCHEDULE FOR PROJECT TASKS